LA-UR- 02-5731

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Submitted to: 2002 Fuel Cell Seminar,
Palm Springs, CA
November 18-21, 2002

TRANSIENT PROX CARBON MONOXIDE MEASUREMENT, CONTROL, AND OPTIMIZATION

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Introduction

Fuel processing systems for low temperature polymer electrolyte membrane (PEM) fuel cell systems require control of the carbon monoxide concentration to less than 100 ppm to 10 ppm in the anode feed. Conventional hydrocarbon fuel processors use a water-gas shift (WGS) reactor to react CO with water to form H_2 and reduce the CO concentration. The CO conversion is limited by equilibrium at the outlet temperature of the WGS reactor. The WGS outlet CO concentration can range from over 1% to 2000 ppm depending on the system and its operating parameters. At these concentrations, CO poisons low temperature PEM fuel cells and the concentrations needs to be reduced further.

One method to reduce the CO concentration uses a preferential oxidation (PrOx), or a similar selective oxidation, reactor to oxidize carbon monoxide. These reactors use air injection, temperature control, and a catalyst to oxidize carbon monoxide preferentially, or selectively, instead of oxidizing hydrogen, a parasitic loss of the fuel cell system fuel. The goal is to reduce the outlet CO concentration to less than 10 ppm in steady-state operation and to less than 100 ppm through transients. Both of these specifications will depend on the PEM fuel cell stack CO tolerance.

Fuel processing systems for both stationary and transportation fuel cell systems may require operation over a range of power levels to meet changing load demands. Maintaining system performance through power changes requires the PrOx reactor to control the CO through those transients, which may involve changes in total flow and gas composition. For automotive fuel cell systems, the startup transient time and the startup energy both need to be minimized for consumer acceptance of these systems.

Furthermore, the design and operation of the PrOx reactor require trade-offs to meet both these transient targets and maintain system efficiency, while also meeting targets for fuel processor weight, cost, volume, and durability. For the PrOx, this requires minimization of the parasitic hydrogen consumption and air injection, use of low cost catalysts on rugged supports, and a reduction in the number of components, actuators, and sensors required to control the reactor. We address some of these issues in the following with a brief description of theory of PrOx operation, a description of the experimental reactor and apparatus, a presentation of experimental results from power and composition transients, and conclusions.

Preferential Oxidation Reactor Design

A PrOx reactor can be used in a fuel processor to reduce its outlet CO concentration to levels that do not compromise the performance of the fuel cell stack. The PrOx removes CO by catalytic oxidation ($CO + \frac{1}{2} O_2 \rightarrow CO_2$) with air injected into the hydrogen-rich reformate stream. Hydrogen oxidation ($H_2 + \frac{1}{2} O_2 \rightarrow H_2O$) is minimized by choosing the catalyst and temperature range so that CO is preferentially or selectively oxidized. The water-gas shift (WGS) reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) and its reverse (RWGS) also may occur over the catalysts used. When the CO concentration is above equilibrium, the WGS reaction can be used to advantage to further remove CO. When the CO is below equilibrium, the RWGS reaction must be prevented to avoid forming more CO. Thus temperature control can be critical both to maintain the selectivity for CO oxidation and to prevent the RWGS reaction. Methanation also may occur on the catalysts used for preferential oxidation. The methanation of CO ($CO + 3H_2 \rightarrow CH_4 + H_2O$) may be used to remove CO. Its usefulness is limited to removing small CO concentrations, because it does so at the expense of hydrogen consumption. The methanation of CO_2 ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) should be avoided by temperature control, because of the added hydrogen consumption and the potential for thermal runaway.

Figure 1 shows a schematic of a staged adiabatic PrOx reactor used to implement these reactions for the removal of CO. Key elements of the reactor are: 1) air injection controlled individually for each stage; 2) interstage heat exchange to control the inlet temperature to a stage; 3) gas distribution and mixing elements to mix the air uniformly into the reformate stream and then to distribute that stream uniformly over the catalyst inlet; and 4) catalysts that are selected for the expected inlet CO concentration range and operating temperature. The number of stages used depends on the expected range of inlet CO concentration, the catalysts used, and the turndown range. Turndown range can be extended in a staged system by turning on and off the air to a stage.

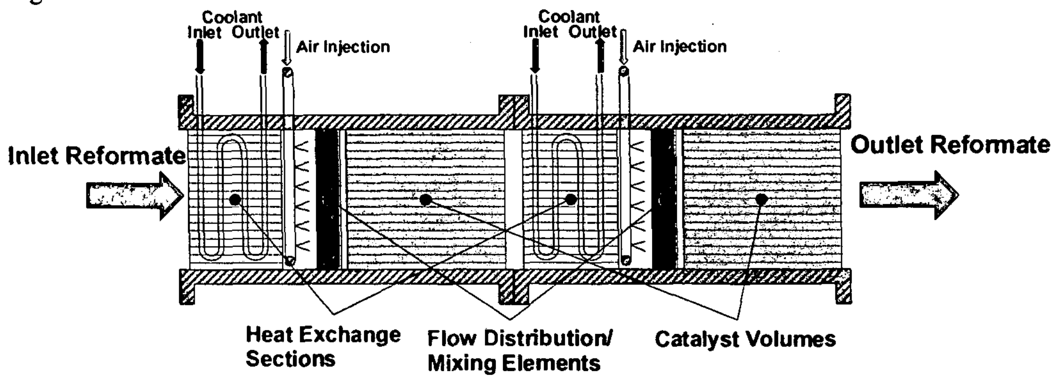

Figure 1. Schematic of a staged adiabatic PrOx reactor system showing the major components.

Figure 2 shows the schematic of an individual stage design used in a modular laboratory PrOx reactor. The design incorporates a replaceable catalyst holder that can hold monoliths, foams, or pellet catalysts. The holder is suspended to minimize the mass in contact with the catalyst in order to reduce thermal conduction losses and to enhance transient response. After exiting the catalyst, the reformate passes over the outside of the catalyst to recuperate heat for a faster warmup. Air is injected into the reformate at the inlet of the heat exchange section to take advantage of mixing over the heat exchange surfaces. The reformate is cooled by heat exchange with a coolant on the outer wall of the reactor. The heat exchange controls the inlet temperature to the next stage. Internal components were fabricated from deep drawn stainless steel to reduce the mass of the internal components for faster transient response.

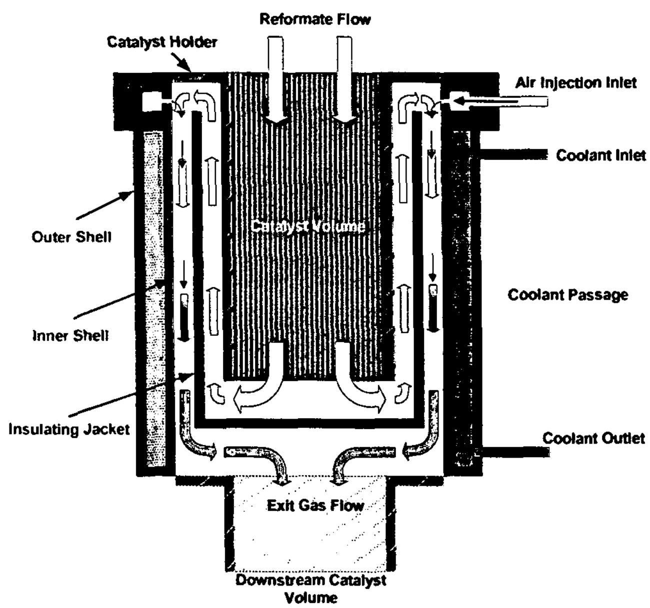

Figure 2. Schematic of cross-section of a laboratory PrOx stage.

Experimental Setup

PrOx reactors and components are tested in a PrOx test facility that can simulate the reformate output from gasoline, natural gas, or methanol fuel processors. The test facility can provide mixtures of the major constituents of reformate, H_2, N_2, CO_2, and H_2O, at automotive-scale flow rates up to a 50 kW net electric equivalent. Minor constituents such as CO are injected to simulate the trace contaminants.

Transient experiments can be conducted by the computer-controlled data acquisition and control system. These experiments can include power, composition, and startup transients. Power transient experiments examined the response and control of changes in the total flow rate that would correspond to changes in power demand from the fuel cell. Composition transient experiments examine the response and control to changes in gas composition such as variations in CO concentration. Such information is useful to determine requirements for detection limits of CO sensors. Startup experiments examine the limitations on PrOx reactor startup transient response.

A four-stage PrOx was used for investigations of power transients and a startup transient with a high inlet CO concentration. The steady-state performance of this 4-stage PrOx has been described previously (1) for the removal of 2% CO to an outlet CO less than 10 ppm. Stages 1 and 2 of this reactor used a commercial Cu/ZnO pellet catalyst for operation at a high inlet CO concentration above 1%. Preferential oxidation of CO occurs in the front portion of the catalyst volume. Then once the oxygen is consumed, the catalyst has sufficient WGS activity to further remove CO. Stage 3 was designed to operate with an inlet CO concentration in the range of 5000 ppm and used a commercial Ru/Al_2O_3 pellet catalyst. With this catalyst, excess air addition and thus increased catalyst temperatures led to CO methanation instead of the RWGS reaction. Stage 4 was designed to operate with an inlet CO concentration in the range of 1000 ppm and used a commercial Pt/Al_2O_3 pellet catalyst. In this CO range, the air addition is small and thus the adiabatic temperature rise is small, so the RWGS reaction can be avoided. The ability to tolerate excess air addition without generating more CO by the RWGS reaction is critical for controlling CO through transients. A single-stage PrOx reactor was used to investigate the response of a single Pt-based catalyst monolith to power, composition, and startup transients.

Power Transients

The response of both the 4-stage PrOx and the single-stage PrOx to a simulated power transient was measured by subjecting them to step transients in the total flow. The step transients were between 10 kW and 30 kW (based on the LHV of the H_2 flow) in a simulated gasoline reformate with 37% H_2, 28% N_2 17% CO_2, and 17% H_2O. The inlet CO concentration was 20,000 ppm for the 4-stage experiment and 2000 ppm CO for the single-stage experiments. Air injection flows were switched between their steady-state flows at the 10 kW and 30 kW levels. The timing of the switch was varied to investigate control of CO through the transient.

The outlet CO response and its control of the 4-stage PrOx were complicated by the interactions between the stages during the step transients. Stage 3 exhibited instabilities in its outlet CO concentration that produced both power and composition transients at the inlet of stage 4. The combination of these transients prevented control of the CO below 100 ppm through the step transient. Based on these results, we focused on examining and controlling step transients in single-stage experiments to decouple the effects produced in a multi-stage PrOx.

In the single-stage experiments, the outlet CO response peak could be maintained below 100 ppm by the air injection leading the main flow step-up transient by 1 second and by the air injection lagging by 1 second on the step-down transient. Figure 3 shows the air flow and CO flow (coincident with the main flow) through the step transients. Figure 4 shows the outlet CO response with a peak below 100 ppm occurring on the down transient. CO formed by the RWGS reaction as the residence time increases over a catalyst at a higher temperature may account for the peak on the down transient. The experimental control resolution was on the order of 1 second, so further fine tuning of the air injection timing was not feasible.

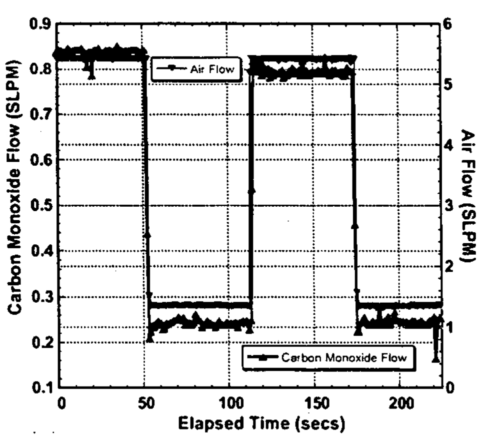

Figure 3. CO and air injection flows through the step transient between 10 kW and 30 kW.

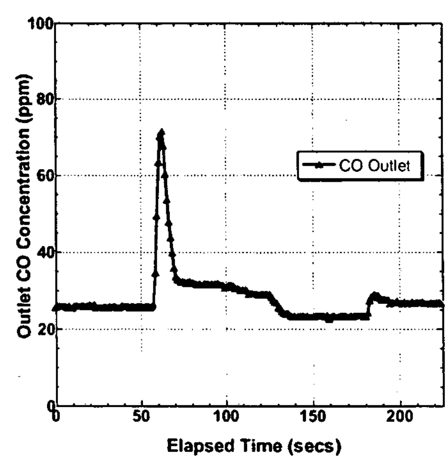

Figure 4. Outlet CO concentration through the step transient between 10 kW and 30 kW.

Composition Transients

Composition transient experiments were conducted by varying the inlet CO concentration at an overall steady flow. The goal was to examine the outlet CO response to inlet variations and then to devise a control method. Initial experiments were conducted with a single-stage PrOx with an inlet gas composition of 38.1% H_2, 27.3% N_2, 15.7% CO_2, and 17.1% H_2O at a GHSV of 38,000 h^{-1}. The inlet CO concentration was varied sinusoidally from 8,000 to 12,000 ppm with a 60 s period. Air injection was held constant for a given air stoichiometry at 10,000 ppm. The outlet peak-to-peak CO concentration was found to decrease with increasing oxygen stoichiometry. Figure 5 shows the outlet CO response for an air stoichiometry of 1.44. The peak-to-peak variation is from 50 ppm to 1350 ppm.

A subsequent experiment was conducted with the same main gas flows with the inlet CO concentration varied sinusoidally between 0 to 2000 ppm. The goal was to test the ability of a second stage to control the outlet CO from the previous experiment. With the air injection flow set to an air stoichiometry of 2.4 for 2000 ppm CO, the outlet CO concentration was held between 5 to 15 ppm. Thus, we could expect that the combination of the two stages could handle an inlet variation from 8,000 to 12,000 ppm without additional control inputs. However, this control simplification comes at the expense of additional hydrogen consumption when the CO concentration is at the lower levels. This concept will be tested with a multi-stage PrOx in future experiments.

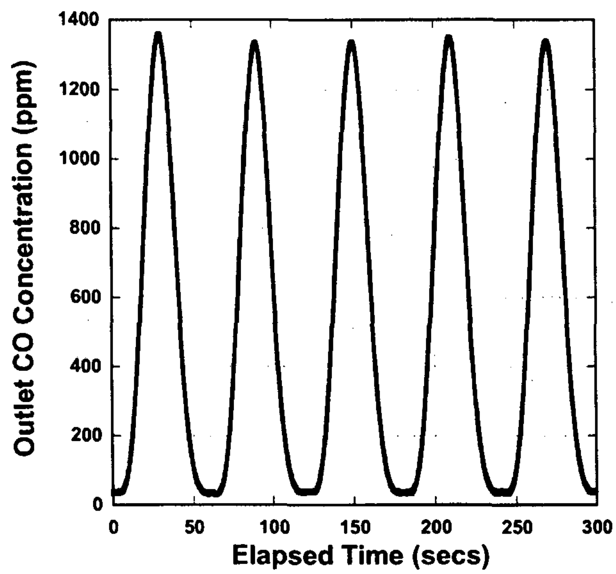

Figure 5. Outlet CO concentration with a sinusoidal variation from 8000 to 12000 ppm with an air stoichiometry of 1.44.

Conclusions

A working laboratory PrOx reactor has been designed and developed based upon a staged adiabatic design. The modular stage design includes features to simplify catalyst replacement and multi-stage configurations. The mass of the internal components was reduced by design to reduce overall startup time and to speed transient response. Commercial pellet catalysts were selected for use in a 4-stage configuration to reduce an inlet 2% CO concentration to an outlet 10 ppm CO concentration. Improvements on this base configuration are being investigated by incorporating monolith-supported catalysts for reduced mass and faster transient response.

Power transient response and control was investigated with single-stage PrOx experiments. Control of the peak outlet CO concentration could be kept to less than 100 ppm by controlling the air injection timing relative to the step transient in the main reformate flow. Thus, control of the outlet CO appears feasible for power transients over the limited turndown ratio investigated. Composition transient response was also investigated with single-stage PrOx experiments. Sinusoidal variations in the inlet CO concentration can be damped out and then potentially eliminated in a second stage by proper selection of the air injection flows. This strategy can eliminate the need for added controls to handle inlet CO variations over a limited range, but does so at the possible expense of added hydrogen consumption. Future experiments will examine the response and control of outlet CO concentrations in multi-stage PrOx configurations.

REFERENCES

1. Michael A. Inbody et al., "Transient Carbon Monoxide Control for PEMFC Applications", *2000 Fuel Cell Seminar*, October 30-November 2, 2000, Portland, Oregon.